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Effects of hydrogen peroxide preoxidation on clarification and reduction of the microbial load of groundwater and surface water sources for household treatment

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ABSTRACT

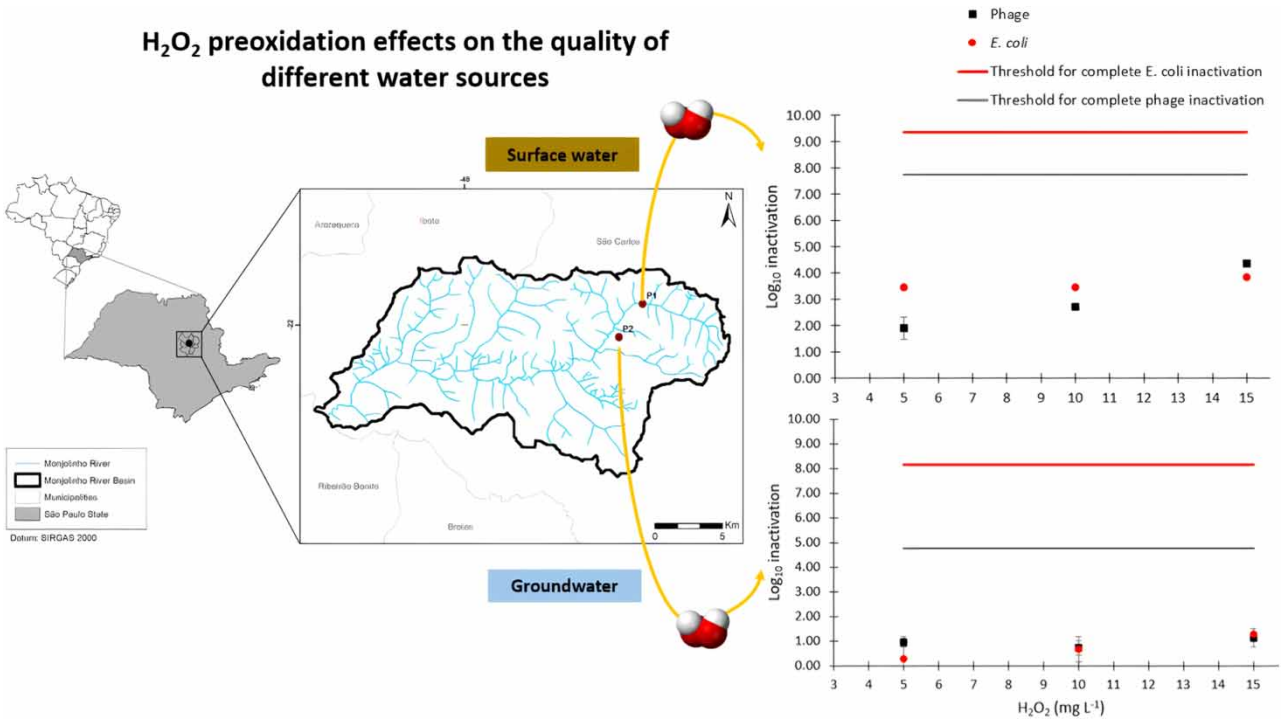
Household water treatment (HWT) technologies are a promising strategy for addressing the waterborne diseases burden. However, in order to be efficient, these are often limited to water quality and require it to not exceed a certain threshold of physicochemical and microbiological contamination. Additionally, some popular HWTs, as chlorination, are related to by-product formation. Preoxidation may improve source water quality, and hydrogen peroxide (H_2O_2) is an oxidant that has not been deeply explored in this specific application, so it could be an innovative approach to HWTs. We investigated effects of H_2O_2 preoxidation in two natural source waters (surface and groundwater), spiked with a high level of microorganisms. Clarification results suggested this pretreatment may improve life of HWTs. Reduction in microbial load of groundwater was considered ineffective, but 5-min H_2O_2 preoxidation at 15 mg L^{-1} led to >4.0 $\log_{10}$ inactivation of Phi X174 coliphage and >3.0 of *Escherichia coli* in surface water. We believe this performance was increased due to the presence of catalysts in the river water. This raised the point that water quality may be not only impairing, but potentially beneficial to the main HWT and characterization is crucial prior to the implementation of any technologies.

Key words: drinking water, indicator bacteria, oxidant demand, Phi X174 coliphage, water quality

HIGHLIGHTS

- 5-min oxidation with H_2O_2 led to >3.0 $\log_{10}$ inactivation of *E. coli* from surface water.
- H_2O_2 preoxidation may improve microbiological quality of surface water prior to other treatments.
- H_2O_2 preoxidation of groundwater for reducing microbiological load is not encouraged at the tested doses.
- Natural catalysts from surface water may have enhanced H_2O_2 preoxidation performance.

GRAPHICAL ABSTRACT



INTRODUCTION

Although access to safe drinking water has been increasing in a global scale, inequalities remain, and household access of specific contexts are often overlooked (UNICEF & WHO 2019; Price *et al.* 2021). According to WHO and UNICEF, water consumption of 159 million people worldwide is supplied directly from untreated surface water (WHO & UNICEF 2017). Most surface water sources are considered unfit for drinking because of either natural and/or anthropogenic influences as in unregulated industrial discharges (Ezeabasili *et al.* 2014) or agriculture activities (Sasakova *et al.* 2018). Although groundwater is traditionally expected to be microbe-free, the presence of indicator bacteria and human pathogens has been reported (Polo-López *et al.* 2019; Chique *et al.* 2020). Bofill-Mas *et al.* (Bofill-Mas *et al.* 2013) gathered worldwide data on contamination with human viral pathogens in different water sources, including river water, lagoons, and groundwater.

Household water treatment (HWT) systems have been emerging as a promising strategy to control waterborne diseases spread in developing countries, particularly when piped service is not available (Ehdaie *et al.* 2020). HWTs consist of on-site treatment technologies, capable of reducing pathogen levels in water sources and making other parameters suitable to potability (Pooi & Ng 2018). However, some of these technologies, e. g. solar disinfection (SODIS), filtration, and others, are limited by the quality of the source water (Rose 2005; Gao *et al.* 2011), particularly when it contains high levels of natural organic matter (NOM) associated to turbidity and color.

NOM removal is therefore essential, as it conveys color and taste to the water, makes it unattractive to consumers, provides substrate for bacterial regrowth in the distribution system and storage, and potentially imparts adsorbed organic and inorganic contaminants, as well as microorganisms (Exall & Vanloon 2000). Such unfavorable conditions may also cause rapid membrane fouling or clogging of filter media, increasing maintenance frequency, and reducing water production (Pooi & Ng 2018), as well as increasing the risk of microorganisms to permeate through (Gwenzi *et al.* 2015). In addition, NOM raises chemical demand and costs in traditional treatments (Xie *et al.* 2016), hence similar impairments apply to HWT technologies.

Pretreatment processes in drinking water production typically rely on screening, preconditioning, and/or other site-specific processes aiming to improve and adapt water quality in such a way that the main technology has its life extended (Panguluri

et al. 2014). Oxidation of organic and inorganic molecules is a common approach for clarification (as well as disinfection), hence chlorination has been a popular method for achieving this goal (Black & Veatch Corporation 2009). Nonetheless, the use of chlorine products in the presence of NOM is associated to the formation of carcinogenic disinfection by-products (DBPs) (Hu *et al.* 2018). An effective approach for containing DBP formation is removing precursors by alternative treatments such as preoxidation with alternative oxidants (Sharma *et al.* 2005; Lin *et al.* 2012). Besides chlorine, permanganate and ozone are the main oxidants for preoxidation of feed water (Zhang *et al.* 2013; Lu *et al.* 2015).

Though it has been widely used in surface disinfection (Brauge *et al.* 2020; Hayrapetyan *et al.* 2020) and has had attention within drinking water treatments (either combined or standalone use) (Guimarães *et al.* 2014; Karel 2018), hydrogen peroxide is not often contemplated in preoxidation (Xie *et al.* 2016). This encourages exploring its potential, particularly considering it may be an alternative for conditioning source waters to household treatment systems that require turbidity and color to not exceed a certain range, as well as to assess removing DBP precursors. Additionally, information on its effectiveness in reducing fecal contaminants in natural waters is lacking in literature. This should be timely within the context of household treatments, whose goal is mostly based on improving water quality from a public health perspective regarding waterborne diseases (Ehdaie *et al.* 2020).

In this scene, the aim of this study was to overall evaluate the effects of H_2O_2 preoxidation of two natural water matrices (surface water and groundwater) in bench-scale batch tests. Pretreatment performance was assessed in terms of physicochemical parameters and microbial load, considering indicator bacteria (*Escherichia coli*) and an enteric virus contamination model (Phi X174). Some of our insights on how water quality influences preoxidation raised a discussion toward potentials of H_2O_2 in HWT.

METHODS

Experimental design

We investigated the effects of hydrogen peroxide preoxidation of different water sources, artificially contaminated with a high microbial load. The microorganisms under analysis were an enteric virus contamination model (Phi X174) and an indicator bacterium (*Escherichia coli*). Details of the biological analyses are further explained.

The first experiment consisted of assessing H_2O_2 initial demand by the water sources, by measuring hydrogen peroxide residuals and pH after two minutes of reaction with 500 mL samples. Another batch of experiments followed, in which a preoxidation setup was simulated within the same conditions, but extending the contact time to five minutes, so that disinfection potential could be evaluated. In these preoxidation tests, physicochemical parameters were then measured, as well as microorganism inactivation. Here, we chose a short exposure time, as a conservative approach, i.e. worst scenario for a household setting, considering preoxidation experiments might range from five up to 100 minutes (Lv *et al.* 2019; Liu *et al.* 2020), depending on the matrix, goal, and available conditions.

Experiments were performed in previously sterilized reagent bottles, wrapped in aluminum foil to prevent photolysis. Magnetic stirring provided the mixture environment. Hydrogen peroxide (30% v v^{-1}) was purchased from Sigma-Aldrich®, USA.

Test waters

This study considered two natural matrices, into which indicator bacteria and an enteric virus contamination model were spiked. Samples were characterized before and after the inoculum. Surface water samples were collected from Monjolinho River, a water source located in the municipality of São Carlos (São Paulo State, Brazil). Groundwater samples were obtained from a well located in the same municipality, accessed from São Carlos School of Engineering (SCSE, USP, Brazil). Collection sites are displayed in Figure 1.

Physicochemical tests and analytical methods

Both test waters were characterized according to Standard Methods (APHA *et al.* 2012) prior to inoculum and after microorganisms were spiked into them. Zeta potential measurements were performed using Zetasizer Nano-ZS (Malvern, UK) at 25 °C. Iron was quantified by USEPA FerroVer® Method using the Iron Reagent Powder Pillows (Hach, USA) analyzed at 510 nm wavelength in a DR 5000 spectophotometer (Hach, USA).

Residual hydrogen peroxide was measured by the ferric thiocyanate method, using the Vacu-vials® kit (Chemetrics, USA) analyzed at 470 nm wavelength. The presence of free chlorine in both raw waters was assessed by the USEPA DPD (N,N-

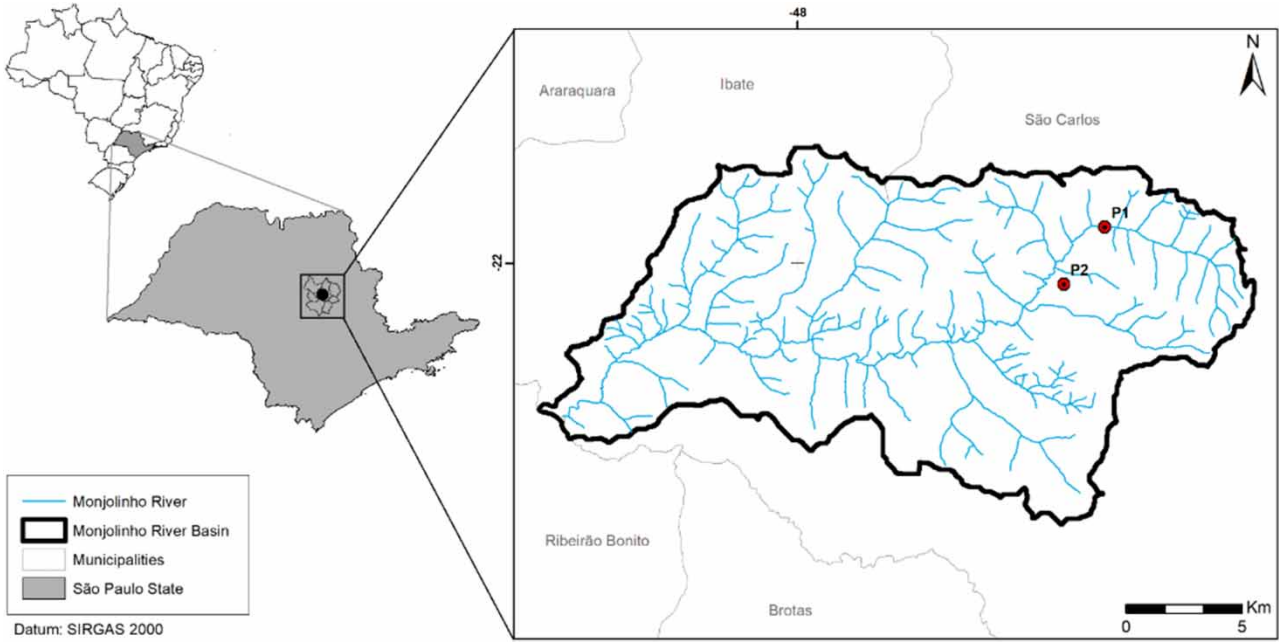


Figure 1 | Location of the collection sites of the test waters P1: Monjolinho River (superficial water source); P2: well from São Carlos School of Engineering.

diethyl-p-phenylenediamine) method using immediate reaction powder pillows (Hach, USA) analyzed at $\lambda = 530$ nm. Both these colorimetric tests were carried out using a DR 3900 spectophotometer (Hach, USA).

After residuals were measured, sodium metabisulfite (Neon, Brazil) was applied for quenching at mass ratio of 3:1 (Moore *et al.* 2021). Microbiological examination was performed as immediately as possible, in order to avoid any possible interferences from residual activity due to slow action (Wang *et al.* 2019) of the quencher.

Target organisms and microbiological analyses

In order to represent fecal contamination, an *Escherichia coli* strain (ATCC® 11229™) was inoculated to the samples as indicator bacterium. Additionally, Phi X174 (ATCC® 13706-B1™) bacteriophage was used as viral indicator of water quality and *Escherichia coli* (ATCC® 13706™) as its host.

Prior to the experiments, the *E. coli* strains and the bacteriophage, originally lyophilized, were eluted, activated, and replicated for preparing master stocks and, subsequently, working stocks. Here, we followed the recommendations from the supplier, as well as peer literature (Fang *et al.* 2014; Kim *et al.* 2017).

Quantification of *E. coli* was performed by the membrane filtration method and colonies were grown in Chromocult® Coliform Agar (Merck, USA), kept at 37 °C for 18–24 hours of incubation. Enumeration was done in terms of CFU 100 mL^{-1}. Aliquots of ATCC® 11229™ leading to an approximate concentration of 10^8 CFU 100 mL^{-1} were inoculated into the test waters.

Phi X174 was counted by soft agar overlay (double-layer agar) method (Kim *et al.* 2017), considering tryptone soya agar (Oxoid™, USA) as culture media. Top agar was prepared with tryptic soya broth (Oxoid™, USA) and bacteriological agar (Sigma-Aldrich®, USA). Samples were filtered in 0.22 μm membranes for purification and subjected to a serial 10-fold dilutions in PBS between 10^{-1} and 10^{-6}. Subsequently, 50 μL of each dilution was added together with 50 μL of the host *E. coli* stock culture in a tube containing 5 mL of top agar and overlayed onto TSA layer. The plates were incubated at 37 °C for 18–24 hours and enumerated in terms of PFU mL^{-1}, according to Equation (1). Natural source waters were inoculated at an approximate order of magnitude of 10^5 PFU mL^{-1}, but there was some die-off of working stocks, as explained in the discussion section.

$$\left(\frac{PFU}{mL}\right) = \frac{1{,}000 \times \textit{average PFUs on plates}}{\textit{volume } (\mu L) \textit{ phage or sample added}} \times \textit{serial dilution PFUs were counted at} \quad (1)$$

Data analysis

PAST 3.2 software (Hammer *et al.* 2001) was used for descriptive and inferential statistics. Pearson's correlation was applied for evaluating the association between physicochemical variables and H_2O_2 concentrations. As for microbiological assessment results, Shapiro-Wilk normality test under a 95% confidence interval determined the probability distribution of the samples, so that normally distributed results were analyzed by one-way ANOVA and the *post hoc* Tukey's test.

RESULTS AND DISCUSSION

Physicochemical characterization and oxidant demand

The general characterization of the water sources is shown in Table 1. It indicates microorganism spiking did not cause any major differences in physicochemical characteristics of the test waters. Differences in water quality obtained for the two sources also draw attention to the importance of such characterization. That is because, even though an HWT may be considered efficient under certain conditions, its ability to improve water safety within a village setting may vary as a function of source water characteristics (Levy *et al.* 2014).

In addition to Table 1, it should be noted that testing for free chlorine carried out for all matrices (both raw and seeded with microorganisms) led to concentrations lower than 0.1 mg L^{-1} Cl_2. Therefore, any chlorine effects on microorganisms, as well as possible interferences in analytical methods, were considered negligible.

Figure 2 shows the residuals found after two minutes of the reaction of hydrogen peroxide to the different matrices, as an inference of initial demand. The oxidant demand represents the consumed disinfectant after it immediately reacted to the sample, considering the presence of competing species, prior to actively reacting towards the inactivation of microorganisms (Freitas *et al.* 2021a, 2021b). It is known that initial demand is directly associated to the water quality (Amerian *et al.* 2019), but no major differences were found when comparing neither H_2O_2 residuals nor shifts in pH of (both seeded) surface water and groundwater, as displayed by Figure 2. That should be explained by the fact that both source waters under test present low levels of organic matter and strong competitors as in sulfide compounds (Wang *et al.* 2017), when compared to more contaminated matrices also often designated to oxidation treatments, e. g. domestic sewage (Medeiros & Daniel 2017; Freitas *et al.* 2021a, 2021b) or agro-industrial wastewater (Sartori *et al.* 2015; Mandro *et al.* 2017). This may come as an advantage from the preoxidation standpoint, as lower doses would be required to directly target microorganisms or provide water clarification, considering the dosed oxidant is supposed to be readily available.

Water clarification

The relative removals obtained for the major physicochemical quality parameters are shown in Table 2. Strong correlations were found for the applied dose and clarification of surface water ($r = 0.93$ for turbidity removal; $r = 0.93$ for color removal) and oxidation of organic matter measured by absorbance at 254 nm wavelength ($r = 0.95$).

Table 1 | Characteristics of the test waters prior to and after inoculum with *Escherichia coli* and Phi X174 phage

		Surface water		Groundwater	
Parameter	**Unit**	**Raw water**	**Seeded water**	**Raw water**	**Seeded water**
pH	–	6.38	6.63	6.21	6.47
Turbidity	NTU	19.00	17.60	0.17	1.16
Apparent color	HU	118.0	113.0	0.9	4.1
Abs 254 nm	–	0.317	0.317	0.004	0.041
Total alkalinity	mg $CaCO_3$ L^{-1}	22.22	NM	28.05	NM
Conductivity	µS cm^{-1}	55.77	187.40	53.37	76.82
Iron	mg Fe L^{-1}	1.44	NM	<0.01	NM
Zeta potential	mV	−16.4	−19.7	−12.9	−14.2
Escherichia coli	CFU 100 mL^{-1}	2.9×10^3	6.7×10^9	ND	2.5×10^8
Total coliforms	CFU 100 mL^{-1}	1.5×10^4	6.7×10^9	ND	2.5×10^8
Phage	PFU mL^{-1}	NM	1.2×10^5	NM	5.9×10^4

ND refers to not detected and NM refers to not measured.

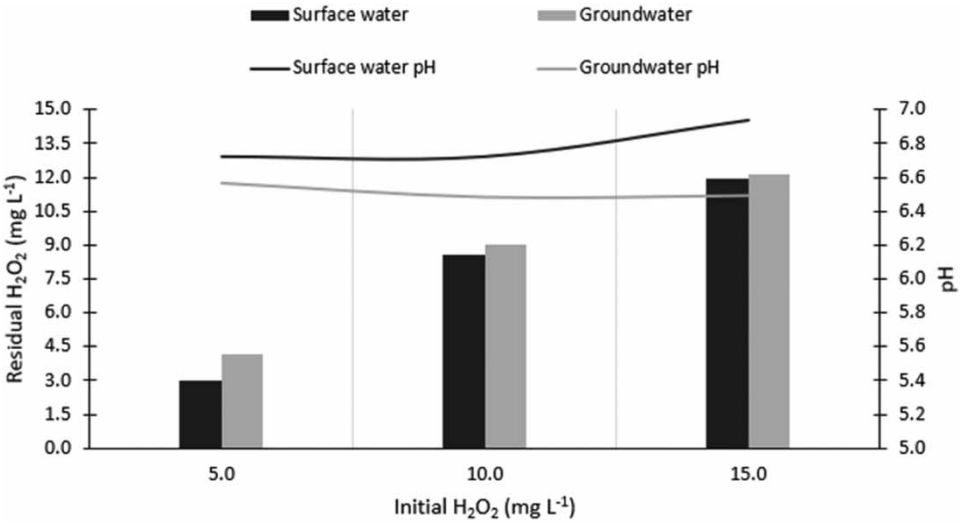


Figure 2 | Residual concentrations of hydrogen peroxide found for surface water and groundwater after two minutes of exposure. Primary y axis refers to columns the secondary ordinate refers to lines.

Table 2 | Hydrogen peroxide residuals and effects in physicochemical characteristics of both seeded surface water and groundwater after 5 minutes, as a function of applied dose

		Surface water			Groundwater		
Parameter		**5 mg L^{-1}**	**10 mg L^{-1}**	**15 mg L^{-1}**	**5 mg L^{-1}**	**10 mg L^{-1}**	**15 mg L^{-1}**
Final pH	–	6.46	6.76	6.74	6.80	6.90	6.84
Final zeta potential	mV	−15.1	−21.3	NA	−12.6	−18.4	−16.7
Turbidity removal	%	28.87	59.01	64.51	79.31	80.76	80.17
Color removal	%	8.01	29.16	50.37	44.44	60.49	62.96
Abs 254 nm reduction	%	1.69	35.42	44.79	14.63	26.83	24.39
H_2O_2 residual	mg L^{-1}	2.76	5.15	5.71	4.17	8.51	8.65

NA refers to data that is not available.

As for groundwater, a Pearson correlation of 0.59 was observed for turbidity reduction. This could be explained by the good quality of the raw water itself, which led to clarification up to almost 100% at the lowest H_2O_2 concentration. Final turbidity obtained for all of the tested doses was <0.3 NTU for groundwater. Removals of color and abs 254 nm led to $r = 0.92$ and 0.94, respectively.

A lower, yet satisfactory, reduction in absorbance at 254 nm was found when compared to turbidity and color removals of both matrices. Differences in absorbance at 254 nm may have occurred by oxidation of carbon, without, however, effectively reducing dissolved organic carbon. It is recommended that total organic carbon is tested coupled to absorbance in the UV spectrum so that alterations in organic matter could be assessed more precisely. Additionally, it should be noted that groundwater presented a low 254 nm absorbance prior to treatment (Table 2). As for surface water, the obtained performance was considered adequate for further treatments. Some HWT systems such as household slow sand filters rely on physical barriers as in non-woven synthetic fabric to adequate physicochemical parameters to their limitations (Faria Maciel & Sabogal-Paz 2018). This pretreatment has led to relative removals of approximately 46% turbidity and 21% apparent color (Freitas *et al.* 2021a, 2021b; Terin *et al.* 2021), falling into similar efficiencies of H_2O_2 preoxidation found in our study.

It should be pointed out that results obtained for zeta potential did not show any trend in groundwater samples after pre-oxidation. As for surface water, although there is unavailable data for the highest hydrogen peroxide tested concentration and a lower value was found at 10 mg L^{-1} H_2O_2, the decrease in absolute zeta potential obtained at 5 mg L^{-1} is suggestive of a reduction in negative charge density of organic matter, a behavior reported in preoxidation literature (Liu *et al.* 2020). This

encourages further research, because, additionally, in the presence of metals such as iron or manganese, preoxidation may cause a rupture in complexes of the metallic ions, resulting in an in-situ production of coagulant (Xie *et al.* 2016).

This endorses that characterization of source water quality is essential for selecting site-specific HWTs, which might be potentially improved by pretreatments such as preoxidation. Within the scope of this research, river water presented iron, as displayed by Table 1. Fe(III) positive charge might contribute to increasing zeta potential, by reducing electrostatic repulsive interaction through electrostatic neutralization (He *et al.* 2015). Considering similar water quality, particularly if a coagulation treatment was planned as the main HWT (Crump *et al.* 2004), optimization of such mechanism is highly recommended in order to take advantage of natural water conditions. Accordingly, other HWTs based on activated carbon, sand, or membrane filtration, for instance, could also be favored. That is because surface charge properties influence adsorption (Hijnen *et al.* 2007) and there is data on attenuation of membrane fouling and decreasing formation potential of DBPs after preoxidation correlating to the reduction of negativity of zeta potential (Khan *et al.* 2020; He *et al.* 2021).

Microorganism inactivation

Figure 3 displays the results obtained for Phi X174 phage and *E. coli* in surface water and groundwater. Baselines indicate the desired level for complete inactivation, considering controlled samples with microorganism spiking, but no oxidation treatment. It is worth noting that although experimental procedures were repeated rigorously, there was some die-off of both *E. coli* and phage spiked into the samples, which is seen by comparing Table 1 to Figure 3. In addition, different microorganism resistance was not assessed due to the variation in order of magnitude between inoculums. The same applies to the effects of dosing in different matrices. Therefore, here we investigated the inactivation of microorganisms, individually, within each matrix.

Considering surface water (Figure 3(a)), the 15 mg L^{-1} hydrogen peroxide dose provided 4.35 ± 0.04 $\log_{10}$ inactivation of phage and an average of 1.90 ± 0.30 $\log_{10}$ at 5 mg L^{-1}. Targeting *E. coli*, the highest reduction amongst the concentrations under study was also obtained at 15 mg L^{-1} H_2O_2 (3.84 ± 0.08 $\log_{10}$), and the lowest, likewise, referred to the 5 mg L^{-1} dose (3.45 ± 0.07 $\log_{10}$). These results suggest preoxidation applications in surface water with similar characteristics to the present one may be useful to reduce disinfectant demand in further steps of treatment, as even low concentrations of hydrogen peroxide led to reduction in microbial load of the matrix. This inference is endorsed by one-way ANOVA, which recommends rejecting the null hypothesis of similar means for the $\log_{10}$ inactivation of phage ($p = 0.0007$), as well as *E. coli* ($p = 0.0019$) at the 95% confidence interval. Tukey's *post hoc* test results are shown in Table 3, indicating that the 15 mg L^{-1} H_2O_2 concentration provided statistically significant results against the other tested doses for $\log_{10}$ reductions considering both target-organisms.

As for groundwater (Figure 3(b)), only 15 mg L^{-1} H_2O_2 reached >1.0 $\log_{10}$ reduction (1.14 ± 0.38 for phage and 1.27 ± 0.04 for *E. coli*), which is still far from a desired dejection in microbial load. Inferential statistics imply similar means for data on

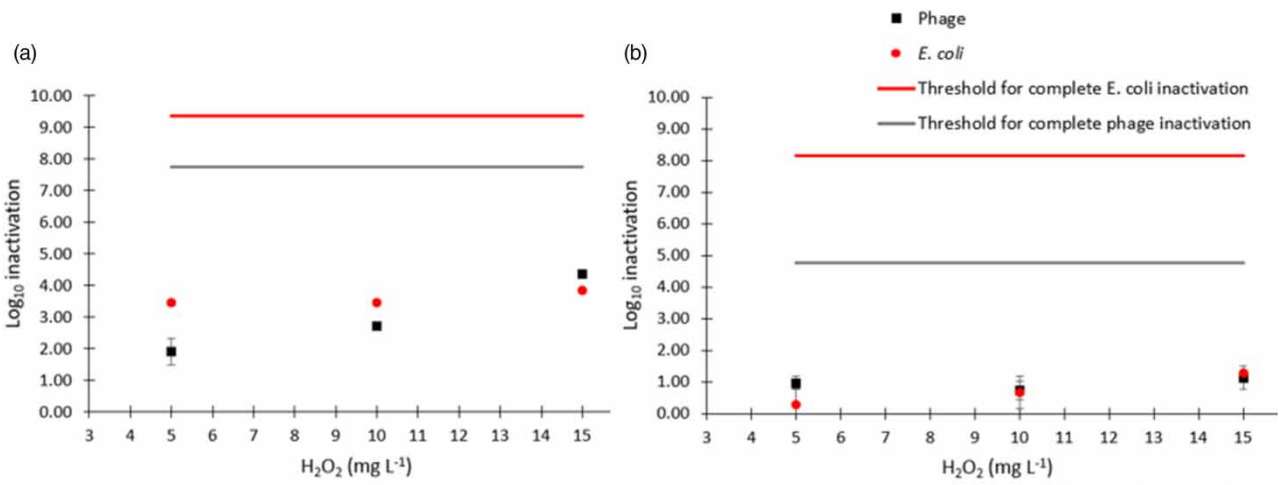


Figure 3 | Mean $\log_{10}$-reductions of *Escherichia coli* and Phi X174 as a function of hydrogen peroxide concentration during 5-min preoxidation in (a) surface water, and (b) groundwater. Error bars refer to standard deviation ($n = 3$) and baselines indicate the $\log_{10}$ levels that would refer to complete inactivation of each inoculum.

Table 3 | p-values of Tukey's pairwise test ($\alpha = 0.05$) for $\log_{10}$ microorganism inactivation of surface water

H_2O_2 concentrations compared	Phage	*E. coli*
5 mg L^{-1} vs. 10 mg L^{-1}	0.0514	0.9706
5 mg L^{-1} vs. 15 mg L^{-1}	**0.0005**	**0.0033**
10 mg L^{-1} vs 15 mg L^{-1}	**0.0071**	**0.0375**

Results in bold refer to significant differences in means.

both phage ($p = 0.3464$) and *E. coli* ($p = 0.1483$) inactivation in groundwater at the different H_2O_2 doses under test. Such low effects on microbial concentration do not encourage hydrogen peroxide preoxidation of this matrix.

Here we recommend a straightforward treatment approach to water sources with quality such as the seeded groundwater from our study. Although the lack of oxidation competitors (Figure 2) suggests oxidative radicals would be more available for microorganism inactivation of this matrix, results obtained have shown otherwise. Additionally, pretreatments would be unnecessary as low NOM levels were found in groundwater (Table 1), hence preoxidation would be an avoidable extra step.

Comparing the inactivation levels obtained in the two source waters, Figure 3 clearly illustrates that preoxidation provided a better performance for inactivating spiked microorganisms from river water. It should be noted that natural waters may contain catalytic species. Iron, copper and zinc, for instance, provide good catalytic activities (Kitanosono *et al.* 2018). By analyzing Table 1, an iron concentration of 1.4 mg Fe L^{-1} was found in the surface water sample. Considering the presence of the catalyst, we believe that a non-intentional Fenton process may have acted during peroxidation, improving disinfection performance in river water. In this process, hydroxyl radicals (·OH), which present powerful oxidation ability, are produced from the reaction between aqueous ferrous ions and H_2O_2 (Polo-López *et al.* 2019), according to:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^0 + OH^-$$

In order to obtain good disinfection rates, higher amounts of iron are usually required (Polo-López *et al.* 2012). However, humic substances may either consume or catalyze the formation of hydroxyl radicals, depending on their concentration and molecular form (Vione *et al.* 2004) Here, we also raise the hypothesis that they may have acted as catalysts to the Fenton process, which is favorable for practical reasons. Considering that reagents are one of the most impairing costs for (Polo-López *et al.* 2019), the presence of natural catalysts in source waters may be advantageous. We highlight this potential, especially if H_2O_2 preoxidation is intended prior to solar disinfection (SODIS) treatments (Villar-Navarro *et al.* 2019; Jin *et al.* 2020), for instance, either providing or improving a photocatalysis setting.

In short, results strongly suggest the influence of natural catalysts in river water, which improved the inactivation performance of H_2O_2 on the target-organisms by giving means to the formation of hydroxyl radicals. It should be noted, additionally, groundwater presented higher total alkalinity compared to the surface water source, which may have prevented the formation of hydroxyl radicals (Burns *et al.* 2012), along with the lack of natural catalysts.

Although H_2O_2 is a thermodynamically powerful oxidant, its reaction rates are typically slow compared to those of free radicals (Burns *et al.* 2012). It is generally believed that microbial inactivation by hydrogen peroxide does not directly result from oxidative properties of its molecular state, but the consequence of the activity of other strongly oxidant chemical species derived from it (Labas *et al.* 2008). In this sense, implementing a preoxidation stage should consider advantages and constraints related to water quality and the main HWT, in order to obtain the best from H_2O_2 potentials within specific settings.

CONCLUSIONS

Hydrogen peroxide was considered efficient in improving physicochemical characteristics of both surface and groundwater. As for surface water, particularly, turbidity and color removals may considerably increase the life of the following HWT.

Reduction in microbial load was surprisingly low for seeded groundwater, which suggests this matrix is suitable for more straightforward treatments as in household disinfection itself. It should be noted that, in our research, a contamination scenario was simulated with microorganism spiking. As for surface water, H_2O_2 preoxidation reduced virus and *E. coli* contamination levels at >4.0 and >3.0 $\log_{10}$, respectively, at the 15 mg L^{-1} dose. This indicates H_2O_2 preoxidation may

improve microbiological quality of highly contaminated surface water, making it less demanding from the main treatment. Here, we hypothesize that iron content of the natural surface water may have provided catalytic activity to the preoxidation.

Our results highlight the importance of evaluating water quality, which can be either impairing or favorable to a HWT implementation. Although design for practical applications of H_2O_2 preoxidation was not within the scope of this study, further research is encouraged for assessing its performance and cost-effectiveness in different conditions, source waters, and coupled to specific HWTs.

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DECLARATION OF COMPETING INTEREST

No potential conflict of interest was reported by the authors.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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